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PLATINUM COMPLEXES OF UNSATURATED SILOXANES AND PLATINUM CONTAINING ORGANOPOLYSILOXANES

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No Drawing. Continuation of application Ser. No. 861,199, Sept. 25, 1969, which is a continuation of application Ser. No. 598,216, Dec. 1, 1966, both now abandoned. This application Apr. 28, 1971, Ser. No. 138,273

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ABSTRACT OF THE DISCLOSURE

Platinum complexes of unsaturated siloxanes are provided which are useful as hydrosilation catalysts. These platinum-siloxane complexes can contain an average of up to about one halogen atom, per gram atom of platinum, which include platinum-siloxane complexes which are substantially free of inorganic halogen. These platinum-siloxane complexes can be made by effecting contact between a platinum halide and an unsaturated siloxane, for example 1,3-divinyltetramethyldisiloxane, and removing available inorganic halogen from the resulting material. In addition, curable organopolysiloxane compositions are provided comprising an organo-polysiloxane polymer and an effective amount of such platinum-siloxane complex.

This application is a continuation of application Ser. No. 861,199, filed Sept. 25, 1969, which in turn is a continuation of application Ser. No. 598,216, filed Dec. 1, 1966, both now abandoned.

The present invention relates to platinum-siloxane complexes of unsaturated siloxanes which are useful as hydrosilation catalysts, and to curable organopolysiloxane compositions containing such catalysts. In addition, the present invention relates to methods for making these materials.

Prior to the present invention, various hydrosilation methods were known for effecting the addition of an organosilicon material, having a hydrogen atom attached to silicon, to an aliphatically unsaturated material having either olefinic or acetylenic unsaturated resulting in the formation of an adduct having a new silicon-carbon linkage. The reaction is illustrated with respect to the olefinic double bond as follows:

$$\equiv SiH + \underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}} \longrightarrow \equiv Si-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}H$$

Many of the known hydrosilation methods involve the employment of a platinum catalyst in the form of a halogenated platinum compound, or finely divided platinum metal. For example, Speier Pat. 2,823,218 utilized chloroplatinic acid as the platinum catalyst. Another method is Bailey Pat. 2,970,150 which shows the employment of platinum metal supported on a finely divided carrier, such as charcoal. Additional methods are shown by Ashby Pats. 3,159,601 and 3,159,662, and Lamoreaux Pat. 3,220,972, all of which are assigned to the same assignee as the present invention.

Although the above-described platinum catalyzed hydrosilation methods provide for valuable results, the parts by weight of platinum metal values, per million parts of hydrosilation mixture, required for effective results, often render these methods economically unattractive. In many instances, for example, substantial amounts of platinum metal values are rendered catalytically inactive and beyond recovery. The loss of platinum values can be aggravated by the fact that the use of excessively high parts

by weight of platinum catalyst are sometimes required to achieve desirable hydrosilation rates. However, it has been found in particular instances that the rate of hydrosilation is sometimes diminished when some of the prior art platinum catalysts are utilized above normal catalyst weight proportions.

Prior to the present invention therefore, platinum catalyzed hydrosilation methods often resulted in the loss of undesirable amounts of platinum metal values. In addition, the limited cure rate provided by the employment of prior art platinum catalyst has often limited the extension of hydrosilation as a cure mechanism in organo-polysiloxane compositions.

The present invention is based on my discovery that significantly improved hydrosilation results can be achieved with certain platinum-siloxane complexes, as defined hereinafter. These platinum-siloxane complexes have available inorganic halogen sufficient to provide for an average ratio of gram atoms of halogen, per gram atom of platinum, having a vlue of up to aboue one. As known by those skilled in the art, conventional platinum halides employed as hydrosilation catalysts have available inorganic halide sufficient to provide for an average ratio of gram atoms of halogen, per gram atoms of platinum having a value of at least about two.

Although I do not wish to be bound by theory, I have found that in order to produce the platinum-siloxane complexes of the present invention, there must be utilized (A) platinum halide, and (B) a complexing material in the form of an unsaturated organosilicon material selected from,

(a) unsaturated silanes of the formula,

(1) $$R_aR'_bSiX_{4-a-b}$$

and

(b) unsaturated siloxanes of the formula,

(2) $$R_cR'_dSiO_{\frac{(4-c-d)}{2}}$$

where R is free of aliphatic unsaturation and selected from monovalent hydrocarbon radicals, and halogenated monovalent hydrocarbon radicals, and R′ is selected from monovalent aliphatically unsaturated hydrocarbon radicals and halogenated monovalent aliphatically unsaturated hydrocarbon radicals, X is a hydrolyzable radical, a is a whole number having a value between 0 to 2, inclusive, b is a whole number having a value between 1 to 4, inclusive, the sum of a and b is equal to 1 to 4, inclusive, c has a value equal to 0 to 2, inclusive, d has a value equal to 0.0002 to 3, inclusive and the sum of c and d is equal to 1 to 3, inclusive.

The platinum-siloxane complexes of the present invention can be made (1), effecting contact between an unsaturated organosilicon material as defined by Formula 1 or 2 above, and a platinum halide, to provide for the production of a mixture having a concentration of available inorganic halogen, which is sufficient to provide for an average ratio of gram atoms of halogen, per gram atom of platinum having a value of at least about two, (2) treating the resulting mixture of (1), to effect the removal of available inorganic halogen, and (3) recovering from (2), a platinum-siloxane complex having available inorganic halogen which is sufficient to provide for an average ratio of gram atoms of halogen, per gram atom of platinum, having a value up to about one.

As used throughout the description of the present invention, the term "available inorganic halogen," will designate halogen that can be detected by a modification of ASTM designation D-1821-63 for "Inorganic Chloride." The procedure employed is substantially as described, except there is utilized in place of acetone, which is the solvent specified in the test, a mixture of glacial acetic acid